relative to dT are consistent with such changes in an S type of pucker.[40] However, there seem to be no steric interactions in a syn pyrimidine nucleoside which are serious enough to preclude an N type of pucker, and thus in general one should expect an N⇌S interconversion in solution for syn as well as anti molecules. It is important to note that our crystallographic data provide no information about the influence of syn pyrimidine bases on a deoxyribose ring with an N-type pucker. Such information can only be obtained from a comparison of syn and anti 2'-deoxyribosides crystallized in the N range. There are many examples of anti,N conformations,[21] but none of syn,N. A more detailed evaluation of the solution conformations should await such data.

In contrast to deoxyribonucleosides, there is no agreement between NMR and crystallographic results for ribonucleosides. In the solid state the conformation of uridine is anti,C(3')endo[25] and that of 6-methyluridine is syn,C(2')endo.[8] On the other hand, NMR data for the latter suggest a shift away from the C(2')endo conformer.[42] Thus, the correlation between the sugar pucker and the syn conformation about the glycosyl bond remains unclear.

Acknowledgments. All crystallographic computations were carried out with programs written by Ahmed et al.[43] Figures 1, 4, and 5 were drawn with the ORTEP program of Johnson.[44] We acknowledge the expert advice of Dr. K. Sadana (Microbiology Department, The University of Manitoba) in the synthesis of m^6dU. The synthesis was made possible by a grant (A6434) from the Natural Sciences and Engineering Research Council of Canada. W.P.N. is grateful to The University of Manitoba for a Manitoba Fellowship.

Supplementary Material Available: Anisotropic temperature parameters and a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

(40) We do not mean to imply that the type S pucker of a syn deoxyriboside in solution is exactly the same as in the crystal structure of m^6dU. The comparison of the solution and solid-state geometries is complicated by the presence of the intramolecular O(5')-H···O(2) hydrogen bond which is present in the solid but not in aqueous solution. Undoubtedly the formation of this bond places some constraints on the sugar which are reflected in the values of P and τ_m. Relevant in this regard are the crystal data for m^6U (Table III). A significant difference in P (10.3°), though not in τ_m (1.1°), is noted between the A form which has a hydrogen bond and the B form which does not. It is likely that the more flexible deoxyribose ring[21,39,41] will be even more distorted by an O(5')-H···O(2) bond. Unfortunately, the only crystal data for syn pyrimidine deoxyribosides other than m^6dU are those of the highly substituted $flac_2^{3',5'}dU$ (Table III) and thus no meaningful comments on the influence of hydrogen bonding on deoxyribose puckering can be made at this time.

(41) Levitt, M.; Warshel, A. *J. Am. Chem. Soc.* **1978**, *100*, 2609-2613.

(42) Schweizer, M. P.; Banta, E. B.; Witkowski, J. T.; Robins, R. K. *J. Am. Chem. Soc.* **1973**, *95*, 3770-3778.

(43) Ahmed, F. R.; Hall, S. R.; Pippy, M. E.; Huber, C. P. *J. Appl. Crystallogr.* **1973**, *6*, 309-346.

(44) Johnson, C. K. ORTEP Report ORNL-3794 (2nd revision); Oak Ridge National Laboratory: Oak Ridge, Tenn., 1970.

Determination of the Lifetime of Singlet Oxygen in D_2O Using 9,10-Anthracenedipropionic Acid, a Water-Soluble Probe

Barbara A. Lindig,[1a] Michael A. J. Rodgers,*[1b] and A. Paul Schaap[1c]

Contribution from the Department of Chemistry and the Center for Fast Kinetics Research, University of Texas, Austin, Texas 78712, and the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received February 11, 1980*

Abstract: A water-soluble singlet oxygen monitor has been used in time-resolved laser photolysis experiments. The disodium salt of 9,10-anthracenedipropionic acid (ADPA) is bleached to an endoperoxide on reaction with singlet oxygen. This change in absorbance was followed by kinetic spectrometry. Singlet oxygen was formed by laser excitation of methylene blue, and the resulting decay of ADPA was first order. Measurement of the rate constant for ADPA bleaching in D_2O as a function of ADPA concentration yielded a line whose slope, $(8.2 \pm 0.5) \times 10^7$ L mol^{-1} s^{-1}, is the bimolecular rate constant for quenching of singlet oxygen by ADPA. The intercept of this line, $(1.9 \pm 0.1) \times 10^4$ s^{-1}, corresponds to the rate constant for natural decay of singlet oxygen in D_2O. The resulting value for τ_Δ, 53 ± 3 μs, substantiates the previously determined values for the singlet oxygen lifetime in D_2O solutions containing ionic surfactant micelles. ADPA shows itself to be a convenient and specific monitor for detecting the presence and decay of singlet oxygen in aqueous systems. To demonstrate this further, the rate constant for singlet oxygen quenching by histidine in D_2O has been determined, using ADPA, to be $(6.1 \pm 0.5) \times 10^7$ L mol^{-1} s^{-1}, a value which is in good agreement with those previously determined using the furan DPBF as singlet oxygen monitor, both in surfactant solution and in alcohol-water mixtures.

The combined discoveries of Khan and Kasha[2a] and of Foote and Wexler,[2b] which implicated an excited state of oxygen in dye-sensitized photooxidations, led to a rapidly growing area of research. Since then, a large number of researchers have been actively involved in the investigation of the reactivity of singlet oxygen toward organic substrates, and more recently examination of its possible role in biological systems.[3] To a large degree, the efforts in the biochemical area have been hampered by the rather limited methods of monitoring the presence and activity of singlet oxygen, especially where water is the major component of the solvent.

In condensed phases the natural lifetime of the $O_2^*(^1\Delta_g)$ state is governed by solvent deactivation via electronic-vibrational energy transfer.[4] In most common polar and nonpolar liquids

(1) (a) Department of Chemistry, University of Texas. (b) Center for Fast Kinetics Research, University of Texas. (c) Wayne State University.

(2) (a) Khan, A. U.; Kasha, M. *J. Chem. Phys.* **1963**, *39*, 2105. *Nature (London)* **1964**, *204*, 241. (b) Foote, C. S.; Wexler, S. *J. Am. Chem. Soc.* **1964**, *86*, 3879.

(3) Krinsky, N. I. In "Singlet Oxygen", Wasserman, H. H., Murray, R. W. Eds.; Academic Press: New York, 1979; pp 597-641. Foote, C. S. In "Free Radicals in Biology", Pryor, W. A., Ed.; Academic Press: New York, 1976; pp 85-133.

(4) Merkel, P. B; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244.

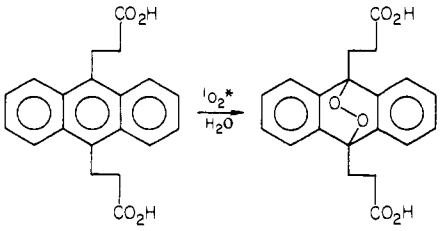
0002-7863/80/1502-5590$01.00/0

(including water) the observed natural lifetimes fall in the range of 1–100 μs. Since the radiative transition in the gas phase has a rate constant of 2.6×10^{-4} s^{-1},[5] the quantum yields of luminescence observed in water (for example) are exceedingly small and far below the detection limit of apparatus capable of time resolution near 1 μs.

Experiments have therefore utilized the chemical reactivity of $O_2^*(^1\Delta_g)$ as a means of its detection. In a number of studies 1,3-diphenylisobenzofuran (DPBF) has been used as a singlet oxygen monitor.[6] The bleaching of its yellow color (λ_{max} 415 nm) has allowed the kinetics of singlet oxygen reactions with it (and other additives) to be followed in both time-resolved and steady-state irradiation experiments. In this respect DPBF has proved to be of much value as a singlet oxygen monitor in organic media.

DPBF is insoluble in water, however, and tends to dimerize and become unreactive toward singlet oxygen in H_2O-rich mixtures.[4] This problem was partly overcome by solubilizing DPBF within surfactant micelles dispersed in D_2O solution, an approach which proved to be extremely successful for the measurement of bimolecular rate constants of several lipophilic and hydrophilic singlet oxygen quenchers.[7-12] These studies indicated that, when the monitoring species (DPBF) and either hydrophobic sensitizer (2-acetonaphthone, pyrene) or hydrophilic sensitizer (methylene blue, eosin) are dispersed as solubilizates in aqueous micellar systems, singlet oxygen generated by energy transfer from the sensitizer triplet state can freely diffuse through the heterogeneous medium. In general, the reaction rate constants compared favorably with those obtained in homogeneous organic solvents. Using this micellar method and laser photolysis we found the natural lifetime of $O_2^*(^1\Delta_g)$ in a D_2O-based dispersion to be 53 ± 5 μs in comparison with earlier estimates of 20 μs obtained by extrapolation from D_2O–methanol mixtures.[4]

The determination of the lifetime of $O_2^*(^1\Delta_g)$ in both light and heavy water is critical for studies on biological oxidations where differences between the rates and extents of oxidation in D_2O and H_2O are often used as criteria for the implication of $O_2^*(^1\Delta_g)$ in such processes.[13] The natural lifetime of singlet oxygen in H_2O has been determined to be 2–4 μs, indicating a strong isotope effect on this parameter.[4,7,8] To eliminate any possibilities that the $O_2^*(^1\Delta_g)$ lifetime is in some way affected by the surfactant micelles and to settle the controversy over its value in D_2O we have used the disodium salt of 9,10-anthracenedipropionic acid (ADPA) as monitoring solute. This compound is water soluble and reacts with singlet oxygen to yield an endoperoxide accompanied by



ADPA ADPA endoperoxide

bleaching of the 400-nm absorption band of ADPA.[14] Using this material in D_2O solution we have performed laser photolysis experiments to measure the natural lifetime of the excited oxygen species in neat D_2O.

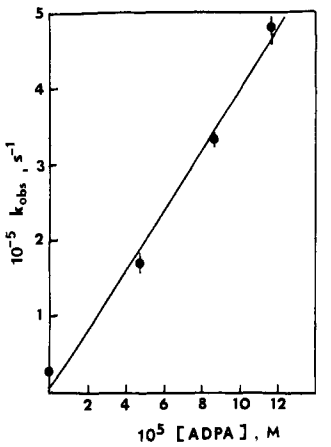


Figure 1. Observed rate constant for decay of $^3MB^*$ as a function of added ADPA concentration ([MB] = 4×10^{-5} M). The bars represent the overall spread of data. The least-squares fit provides a slope of 4×10^9 L mol^{-1} s^{-1}.

Experimental Section

Deuterium oxide (Bio-Rad 99.8 atom %), methylene blue (J. T. Baker), and DL-histidine (Sigma) were obtained commercially and used as supplied. Light water was double distilled, once from potassium permanganate. ADPA (disodium salt) was prepared and purified by B. Kaskar at Wayne State University. (Details of the synthesis and purification are given in ref 14.) Solutions were prepared by normal volumetric techniques in a darkened laboratory. ADPA solutions were prepared by warming and stirring the solid material in water. Photolysis was carried out at ambient temperature (ca. 21 °C) and under an atmosphere of oxygen except where stated.

Methylene blue (MB) was chosen as sensitizer. In water it absorbs red light (λ_{max} 660 nm) to populate the triplet state via an intersystem crossing transition with a quantum yield of 0.52.[15] The excitation source was a Phase-R DL-2100 C dye laser operating with Rhodamine 640 in ethanol in the dye cell. No tuning elements were incorporated in the cavity and thus the whole emission band of the dye (λ_{max} 650 nm) was incident on the target solution. The pulse width was measured at 525 ns (fwhm). Energies of up to 0.5 J/pulse were obtainable with this system. For the current experiments less than 20 mJ was allowed to be incident on the target solution.

Methylene blue triplet state in aqueous solution at pH near 7 absorbs visible light (λ_{max} 420 nm). Its natural lifetime in oxygen-free water (τ = 30 μs) is severely reduced by O_2 saturation (1.4×10^{-3} mol L^{-1}) to 0.38 μs. This reaction produces $O_2^*(^1\Delta_g)$ which can react with ADPA (or added quenchers) resulting in loss of the absorbance of ADPA at 400 nm. The time evolution of this bleaching was followed by using the computer-controlled kinetic spectrometer at the Center for Fast Kinetics Research which has been described.[7]

Results

(i) **MB and ADPA in H_2O, No Oxygen.** In H_2O solutions containing methylene blue (4×10^{-5} M) and ADPA (1×10^{-4} M) no indication of ground-state association was found—the absorption spectrum was the simple sum of the bands for each compound alone. When such solutions were deaerated by N_2 saturation and subjected to laser flash excitation at 650 nm, the methylene blue triplet state, observed at 400 nm, decayed more rapidly than in the absence of ADPA. Over the range of 50–150 μM ADPA the decay of $^3MB^*$ was exponential and first order in ADPA. (The laser beam was attenuated to minimize the contribution of triplet–triplet annihilation to the decay.) The slope of the plot of observed rate constant vs. ADPA concentration (Figure 1) was $(4.0 \pm 0.5) \times 10^9$ L mol^{-1} s^{-1}, which corresponds to the bimolecular rate constant for quenching of methylene blue triplet by ADPA. No significant amount of bleaching of the ADPA was observed under these conditions.

(5) Badger, R. M.; Wright, A. C.; Whitlock, R. F. *J. Chem. Phys.* **1965**, *43*, 4345.
(6) Many examples of the use of DPBF by various workers for the monitoring of singlet oxygen kinetics are reviewed in Wasserman, H. H., Murray, R. W., Eds. "Singlet Oxygen"; Academic Press: New York, 1979; Chapters 4, 5, 12.
(7) Lindig, B. A.; Rodgers, M. A. J. *J. Phys. Chem.* **1979**, *83*, 1683.
(8) Gorman, A. A.; Rodgers, M. A. J. *Chem. Phys. Lett.* **1978**, *55*, 52.
(9) Matheson, I. B. C.; Lee, J.; King, A. D. *Chem. Phys. Lett.* **1978**, *55*, 49.
(10) Lindig, B. A., unpublished results.
(11) Usui, Y.; Tsukada, M.; Nakamura, H. *Bull. Chem. Soc. Jpn.* **1978**, *52*, 379.
(12) Miyoshi, N.; Tomita, G. *Photochem. Photobiol.* **1979**, *29*, 527.
(13) Foote, C. S. In ref. 6, pp 139–171.
(14) Schaap, A. P.; Kaskar, B.; Marnett, L. J.; Sulikowski, S., submitted for publication.
(15) Nemoto, M.; Kokubun, H.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 123.

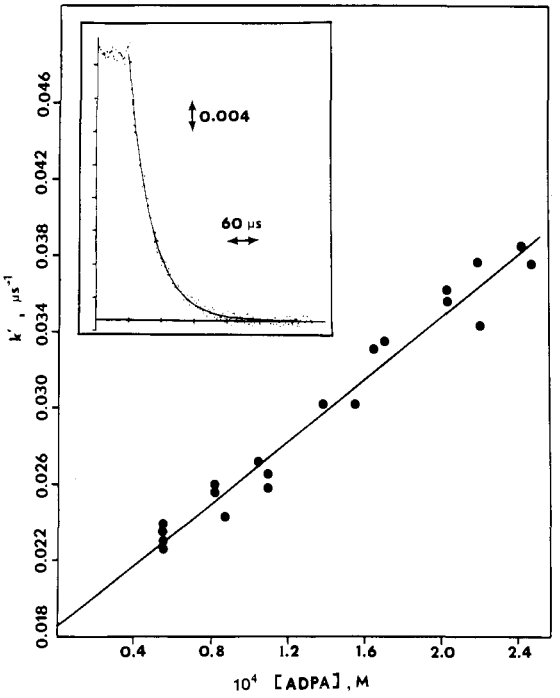


Figure 2. Plot of k' vs. [ADPA]. Each point is the average of at least eight determinations. The least-squares fit yields a slope of (8.2 ± 0.5) × 10^7 L mol^{-1} s^{-1} and an intercept of 0.019 ± 0.001 μs^{-1}. Inset: typical decay curve (absorbance vs. time) shown for [ADPA] = 5.5 × 10^{-5} M. Dots are experimental data; curve is computer-fitted exponential with k' = 0.0227 μs^{-1}.

(ii) MB and ADPA in D_2O, Oxygen Saturated. Solutions prepared in D_2O, containing varying concentrations of ADPA (0.5–2.5 × 10^{-4} M), were oxygen saturated and excited in a similar manner. Under these conditions the methylene blue triplet–triplet absorption decayed very rapidly (see above) and was followed by a substantial bleaching, which was due to the removal of ADPA by its reaction with singlet oxygen. (A typical curve is shown in Figure 2.) No significant amount of ADPA bleaching was evident on saturation with nitrogen. The curves for bleaching at 400 nm were analyzed kinetically and found to be first order. In each case, the extent of bleaching of ADPA was less than 10% of the total ADPA absorbance prior to the flash. A plot of the observed first-order rate constant (k') vs. ADPA concentration was linear with an intercept of 0.019 ± 0.001 μs^{-1} and a slope of (8.2 ± 0.5) × 10^7 L mol^{-1} s^{-1} (Figure 2).

(iii) **Histidine.** When histidine was added in varying concentrations to solutions containing a constant ADPA concentration, the rate constant k' was observed to increase linearly with the histidine concentration. These results are shown in Figure 3; a line of slope (6.1 ± 0.5) × 10^7 L mol^{-1} s^{-1} was obtained by a least-squares fit to the data.

Discussion

Under typical conditions of these experiments, with concentrations of 1.4 × 10^{-3} M oxygen and 1 × 10^{-4} M ADPA, approximately one-fourth of the methylene blue triplets will be removed by ADPA, with the remainder going to form singlet oxygen. The following scheme is proposed:

$$^3MB^* + {}^3O_2 \xrightarrow{k} MB + {}^1O_2^* \quad (1)$$

$$^3MB^* + ADPA \xrightarrow{k_a} \text{products} \quad (2)$$

$$ADPA + {}^1O_2^* \xrightarrow{k_c} \text{ADPA endoperoxide} \quad (3)$$

$$ADPA + {}^1O_2^* \xrightarrow{k_p} ADPA + {}^3O_2 \quad (4)$$

$$^1O_2^* \xrightarrow{k_d} {}^3O_2 \quad (5)$$

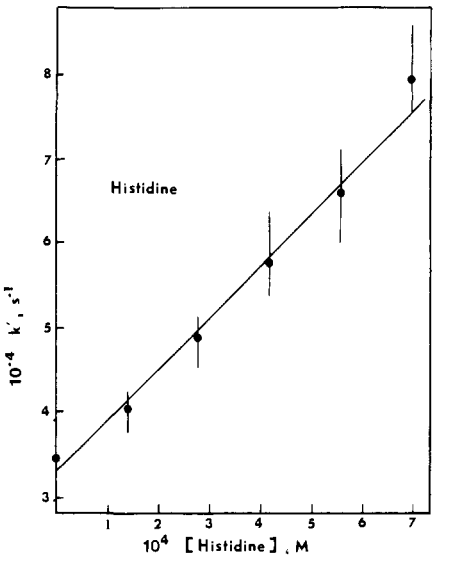


Figure 3. Plot of k' vs. [histidine]. [MB] = 4 × 10^{-5} M, [ADPA] = 1.8 × 10^{-4} M. The bars indicate the overall spread of measured values. A slope of (6.1 ± 0.5) × 10^7 L mol^{-1} s^{-1} results from the least-squares fit.

The products of reaction 2 are not known. If, however, energy transfer occurs, it is possible that any ^{3}ADPA* formed will proceed to sensitize singlet oxygen in a manner analogous to step 1. The loss of ADPA in reaction with $^1O_2$* is then given by

$$-d[ADPA]/dt = k_c[ADPA][{}^1O_2^*] = k_c[ADPA][{}^1O_2^*]_0 e^{-(k_d + k_r[ADPA])t} = k_c[ADPA][{}^1O_2^*]_0 e^{-k't}$$

where $k_r = k_p + k_c$ (the sum of both physical and chemical modes of quenching of $^1O_2$* by ADPA), $k' = k_d + k_r[ADPA]$, and $[^1O_2^*]_0$ is the $^1O_2$* concentration prior to any appreciable loss in steps (3)–(5). Thus, provided that the overall change in [ADPA] is small (<10%), and first-order kinetics are obeyed, the plot of k' vs. [ADPA] should yield an intercept of $k_d(=1/\tau_\Delta)$ and slope of k_r. The data in Figure 2 yield τ_Δ (the singlet oxygen lifetime) = 53 ± 3 μs and k_r = (8.2 ± 0.5) × 10^7 L mol^{-1} s^{-1} in D_2O solution.[16]

The fact that, even though ADPA quenched the MB triplet very efficiently, no significant bleaching was observed under oxygen-free conditions argues against the possibility that this reaction was occurring via a type I mechanism. (Corroboration was provided by the fact that the yield of ADPA bleaching decreased with increasing ADPA concentration.) Further, the observation of the dependence of k' on added histidine concentration serves to confirm that singlet oxygen kinetics are indeed being monitored.

The value for τ_Δ derived from these experiments corresponds exactly to the value of 53 ± 5 μs obtained for D_2O solutions containing micelles composed of sodium dodecyl sulfate, cetyltrimethylammonium bromide, or sodium laurate, in which DPBF was used as monitor for singlet oxygen.[7] Clearly such solutes as these ionic surfactants have no effect on the lifetime of O_2*($^1\Delta_g$) and the micellar technique can be effectively used in situations where it is necessary to solubilize substrates for reasons of hydrophobicity. Caution must, however, be exercised in the choice of surfactants; those named above have been shown to be inert, but others (nonionic surfactants of the poly(ethylene oxide) type) are weakly reactive.[7] No data yet exist for the way in which biological assemblies (e.g., phospholipid vesicles) modify the situation, although preliminary results indicate that unilamellar

(16) To date, no quantum-yield measurements have been performed to determine the relative contributions of k_c and k_p to the total quenching by ADPA (k_r). Therefore, k_r represents a maximum value for the bimolecular rate constant for production of the endoperoxide.

liposomes of egg lecithin are unreactive toward $O_2^*(^1\Delta_g)$ in D_2O suspension.[17]

The use of ADPA provides an alternative to the bilirubin method[18] which has been applied only to alkaline solutions, although Moan and Wold have recently reported that singlet oxygen reacts with certain heterocyclic amines in aqueous solution to produce ESR-detectable nitroxy radicals.[19] While the study of singlet oxygen in aqueous systems was previously deterred by the lack of solubility of DPBF in the medium, the use of ADPA overcomes this difficulty. Further, ADPA has the added advantage that it is somewhat more specific than DPBF for reaction with singlet oxygen: it has been shown that the endoperoxide product is not produced by interaction of ADPA with other common oxidizing species,[14] whereas DPBF has been shown to be sensitive to a number of other oxidizing species, including ground-state oxygen.[20]

As with DPBF, when an added singlet oxygen quencher Q is added to the ADPA system, an additional decay mode must be incorporated, i.e.,

$$k' = k_d + k_r[\text{ADPA}] + k_q[\text{Q}]$$

The measurements illustrated in Figure 3 yield a value of k_q (=the slope of the line) of $(6.1 \pm 0.5) \times 10^7$ L mol^{-1} s^{-1} for the quenching of singlet oxygen by histidine. This value is comparable to values determined in micellar solutions in D_2O ($(5.9 \pm 0.5) \times 10^7$ L mol^{-1} s^{-1} in both sodium dodecyl sulfate and cetyltrimethylammonium bromide solutions[10]) and methanol/H_2O solution (5×10^7 L mol^{-1} s^{-1}),[21] using DPBF as the singlet oxygen monitor. (Note that k_q is the sum of the rate constants for physical and chemical quenching of singlet oxygen by histidine.)

The experimental methods used here and earlier for measuring τ_Δ were confined to systems in neat D_2O, or D_2O-rich mixtures with H_2O. The reason for this concerns the value of τ_Δ in H_2O, which is probably at least one order of magnitude lower than in D_2O.[4,7,13,22] To perform experiments using ADPA in neat H_2O comparable to those shown in Figure 2 would necessitate using an ADPA concentration range of $0.5 \rightarrow 2.5 \times 10^{-3}$ mol L^{-1} to ensure that reactions 3 and 4 competed effectively with (5). Unfortunately ADPA is not sufficiently water soluble to achieve this range.[23] These comments are, of course, only applicable to the time-resolved technique used here. Steady-state irradiation methods such as used elsewhere[6] can be effectively used where solute concentrations are such that reaction 5 is accounting for most of the $O_2^*(^1\Delta_g)$ decay. In such situations the low quantum efficiency of ADPA removal can be effectively offset by long irradiation times, allowing buildup of the reaction to measurable levels. Care must be taken, however, to ensure that the relative concentrations of ADPA and O_2 are such that the large majority of sensitizer triplet states are quenched by oxygen, thus avoiding possible loss of ADPA due to reaction with sensitizer triplet.

An attempt was made to evaluate τ_Δ in H_2O in which experiments were performed by using H_2O/D_2O mixtures in a manner analogous to previous determinations in surfactant solution.[7] That is, solutions were prepared with a constant concentration of MB and ADPA, and with an increasing mole fraction of H_2O in D_2O. The rate constant k' was measured for solutions with 0.0–0.15 mole fraction of H_2O in D_2O. (At higher proportions of H_2O, the extent of bleaching of ADPA was too small to obtain accurate kinetic fits.) Extrapolation to 100% H_2O and correction for the contribution to k' due to k_r[ADPA] led to a value of 3.1×10^5 s^{-1} for k_d in H_2O. Because of the large uncertainty in this value due to the extent of extrapolation we can only report an estimate of 3 ± 1 μs for τ_Δ in H_2O in these experiments. This value does, however, approximate that evaluated (4 μs) from H_2O/D_2O mixtures containing CTAB (cetyltrimethylammonium bromide) micelles with DPBF as monitor.[7]

It is apparent from the experiments described here that ADPA can be successfully used in aqueous systems for determining kinetic parameters of singlet oxygen reactions.[24] As such it offers a helpful alternative to the use of micelle-bound hydrophobic monitoring solutes (e.g., DPBF).

Acknowledgments. We acknowledge the assistance of B. Kaskar in the synthesis of the disodium salt of 9,10-anthracenedipropionic acid. A.P.S. acknowledges the support of NIH Grant CA-15874. B.A.L. and M.A.J.R. thank the Marathon Oil Co. and NIH (Grant GM-24235) for partial support of this research. The Center for Fast Kinetics Research is supported by NIH Grant RR-00886 from the Biotechnology Branch of the Division of Research Resources and by the University of Texas at Austin.

(17) Bates, A. L.; Rodgers, M. A. J., unpublished observations.
(18) Matheson, I. B. C.; Etheridge, R. D.; Kratowich, N. R.; Lee, J. *Photochem. Photobiol.* **1975**, *21*, 165.
(19) Moan, J.; Wold, E. *Nature (London)* **1979**, *279*, 450.
(20) Le Berre, A.; Ratsimbazafy, R. *Bull. Soc. Chim. Fr.* **1963**, 229.
(21) Nilsson, R.; Merkel, P. B.; Kearns, D. R. *Photochem. Photobiol.* **1972**, *16*, 117.
(22) Nilsson, R.; Kearns, D. R. *Photochem. Photobiol.* **1973**, *17*, 65.
(23) The limit of ADPA solubility in aqueous solution was found to be about 3×10^{-4} M, although somewhat higher concentrations can be achieved in alkaline solutions.
(24) Subsequent to the completion of this work, an account appeared of the use of a similar compound (anthracene-9,10-bis(ethanesulfonic acid)) in steady-state experiments.[25] The reported reactivity of this compound toward singlet oxygen is similar to that of ADPA.
(25) Botsivali, M.; Evans, D. F. *J. Chem. Soc., Chem. Commun.* **1979**, 1114.